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To: Dr. D. Mills
Director of Research

A METHOD OF MEASURING CF_3T ACTIVITY DEVELOPED FOR LASER-BASED TRITIUM SEPARATION

H.D. Morrison

The development of laser-based tritium separation at Ontario Hydro Research Division requires experiments on the dissociation of tritiated trifluoromethane, CF_3T. Analysis of the dissociation involves measurements of the changes in concentration of CF_3T in CF_3H by measuring the specific activity of the CF_3T. We employ a modified tritium-in-air monitor built especially for Ontario Hydro by Overhoff & Associates. The instrument can measure from 0.003 to 13 ppm with a precision of less than 0.5% on a minimum gas sample size of 5000 torr-ml. In this report we describe the technique and analytical tools developed to use this instrument most effectively.

1. INTRODUCTION

The process of laser-based tritium separation being developed at Ontario Hydro is based on the infrared multiphoton dissociation of tritiated trifluoromethane, CF_3T [1]. In this process, a gas-phase mixture of CF_3T in CF_3H is exposed to the infrared beam of a CO_2 laser. The CF_3T absorbs many photons and dissociates into two products, TF and C_2F_4. Some of the CF_3H also dissociates to produce HF and C_2F_4. As the dissociation process is isotope selective the tritium concentration is highly enriched in the TF/HF product with respect to the feed concentration of CF_3T in CF_3H. To characterize the dissociation process in our experiments, we measure changes in the concentration of CF_3T in CF_3H. For a complete analysis of dissociation we also need to know the changes in concentration of the C_2F_4 product. At the moment the two measurements must be performed on separate instruments but they may eventually be combined on one instrument. This report describes the instrument and the technique we apply to measuring tritium concentrations in CF_3H.

The initial concentration of CF_3T in CF_3H is usually less than 1 part per million (ppm). To measure these concentrations in the gas phase we employ a tritium-in-air monitor designed and built especially for Ontario Hydro by Overhoff & Associates, Inc. of Cincinnati, Ohio. This instrument, known simply as the Overhoff in our laboratory, measures the radioactivity of a tritiated gas in a static cell. The Overhoff has proved to be reliable and reproducible for measuring CF_3T activity, especially for relative measurements, as required by the laser dissociation research. The absolute calibration of the Overhoff is not well known. This report describes the technique and analytical tools developed to use the Overhoff most effectively.

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2. INSTRUMENT CONSTRUCTION

The heart of the Overhoff is an ionization chamber consisting of a brass cylinder closed at both ends and a thin metal rod running down the centre. A tube connection with an O-ring seal in the side of the cylinder connects the chamber through a valve to the gas rack where all the dissociation experiments are performed. The total volume of the chamber and tube up to the valve is 61.4 ml. Gas admitted to the chamber is partially ionized by tritium decay inside the chamber. A positive bias voltage on the central rod attracts the negative ions, creating a current that is processed into a voltage signal by the counting electronics. Although the Overhoff was intended to work with air in the chamber, it is indeed fortuitous that CF_3H works well as a counter gas: it neither quenches the ionization nor causes avalanche breakdown.

The voltage signal appears on an analogue meter on the front panel and through banana plug connections on the back panel. The front panel meter indicates a value between 0 and 1 for three ranges selected by a front panel switch. The switch selects a full-scale range of 1 Ci/m^3, 0.1 Ci/m^3, or 0.01 Ci/m^3. The back panel connection provides a voltage level between 0 and 10 V that can be read by a voltmeter or a chart recorder. The Overhoff works from line voltage turned on at the front panel with an indicating-light pushbutton. A separate toggle switch turns the chamber on and off. As the unit works best when it is warm and dry, we keep the power on all the time but only turn on the chamber when making measurements. A built-in dessicator, consisting of a plastic tube threaded as for an automotive spark plug and filled with dessicant, also helps to keep the electronics dry. Instability in the Overhoff signal reading outside the normal range of variation may be due to moisture in the electronic circuits. When this condition occurs we replace the dessicant tube.

The Overhoff signal can be zeroed with a zero adjust knob located on the front panel. The knob has a lock ring to prevent inadvertent changes. To find the zero signal level turn the chamber on, evacuate the chamber, and select the 0.01 Ci/m^3 scale.

3. TECHNIQUE

The Overhoff was probably intended to be used at a fixed given pressure, at which the front panel reading would correspond correctly, within a calibration factor, to the activity of the gas sample in units of Ci/m^3. To achieve high precision with this method requires careful attention to the zero of the Overhoff, to the temperature of the Overhoff chamber, to the zero of the pressure gauge, and to setting the correct pressure of the sample. Furthermore, this method can severely restrict the minimum sample size that can be analyzed, depending on the given pressure. Fortunately, these limitations can be overcome by analyzing the pressure dependence of the Overhoff signal for a gas sample. The response of the Overhoff is linear with pressure from a few torr up to several hundred torr. A simple theory of the operation of the Overhoff shows that the slope of the linear region is proportional to the concentration of the activity in the gas sample. The problem then was to find the limits of the pressure range where the response is linear and then to calculate the slope of the best-fit straight line in that range.

The technique for most effective use of the Overhoff was established by analyzing 28 data sets of signal recorded as a function of pressure in the chamber. These data sets, labelled DS#1 through DS#28, are compiled in a binder of notes on the Overhoff analysis. The first two data sets correspond to two different samples of CF_3T, one made here at Research Division and the other made by Amersham, both recorded on 16 February 1988. The results were compared to measurements of these samples on a gas chromatograph equipped with a radiographic detector [2]. The other 26 sets were recorded between 15 August 1986 and 26 March 1987 during a series of dissociation experiments.

Each gas sample to be analyzed was cryo-trapped, using liquid nitrogen as the coolant, into a 5-ml side-arm cell. This cell is connected through a valve to a 1000-torr pressure gauge (MKS capacitance manometer) and to the Overhoff to provide a minimum volume, and maximum pressure,

for gas expansion into the Overhoff. These components are sealed off from the rest of the gas rack by another valve. The total volume containing the gas sample, including the manometer, the side-arm cell, the adjacent section of gas rack and the Overhoff chamber, is 85.9 ml. Usually the sample is allowed to thaw and expand into the Overhoff to obtain the signal for the peak pressure. Then, the pressure dependence is obtained by cryo-trapping the sample back into the side-arm bit by bit. The pressure must be constant for each reading. It is also possible to expand the gas into the Overhoff bit by bit to measure the signal as a function of increasing pressure, although this procedure is more difficult. Subsequent comparison of the two methods, evacuation or expansion, reveals no systematic difference in the slopes of the linear fits.

For all the data sets, the front panel signal of the Overhoff was recorded as a function of pressure in the chamber. In addition to the front panel readings, a digital voltmeter (DVM) was used to read the Overhoff signal from the back panel in DS#2 and in the sets DS#8 through DS#28. These 22 data sets were used to determine the best interpretation of the Overhoff signal as a function of pressure as well as to calibrate the back panel voltage to the front panel signal. The DVM display is easier to read than the front panel because the signal fluctuates every few seconds. One reading requires about 10-20 seconds to average the value by eye and estimate the error range. The repeatability of the measurements reveals that the random errors are small.

All the data sets reveal a common pattern of Overhoff signal as a function of pressure. Figure 1 shows a typical example. As mentioned above, the response is generally linear and the problem was to determine the best regime for analyzing the linear response. In the pressure range of 30 to 400 torr, the response is linear with a positive pressure intercept at zero signal. In the pressure range below 30 torr, the response bends away from the straight line to intersect the origin, i.e. zero signal at zero pressure (except as noted later with respect to a residual signal). At pressures above 400 torr, the signal response saturates with pressure and bends below the linear response.

The optimum limits to the linear regime, i.e. 30 and 400 torr, were determined from an analysis of linear fits to the DVM readings as a function of pressure in the 22 data sets, DS#2 and DS#8 through DS#28. The fitting procedure, described in detail below, is a weighted least-squares linear fit with weights derived from estimated errors in both the signal and the pressure readings. For each fit, the reduced χ^2 and the probability of the reduced χ^2 were calculated. Following the discussion of Press *et al.*[3], 0.01 was selected as the minimum allowable probability for the reduced χ^2. A compilation of the pressure ranges for each data set then provided an estimate of the optimum pressure range for a linear fit. A measure of success of the selected pressure range is that the reduced χ^2 lies close to 1 in subsequent fits to data. Note that the minimum pressure range to assure reasonable precision in the measurement is 30 to 60 torr. This sets a lower limit of about 5000 torr-ml at room temperature for the size of gas sample.

4. THEORY

The Overhoff signal is observed to be linear as a function of pressure over a wide pressure range. Within this range of 30 to 400 torr the Overhoff chamber behaves as a proportional counter. Above 400 torr, the signal saturates, indicating some quenching of the ionization. Going to pressures below 30 torr the signal is nonlinear. The straight line extrapolated from the linear region has a positive pressure intercept of about 10 torr, while the signal varies smoothly to zero at zero pressure. The pressure intercept arises because a fixed amount of gas does not contribute to the signal, independent of pressure. Physically, there is a boundary layer of gas near the walls of the chamber in which the ionization is quenched, either by the wall or by adjacent gas. This boundary layer is not fully established until the pressure reaches about 30 torr: at this point one third of the gas is quenched. Increasing the pressure beyond 30 torr, however, does not change the number of moles of gas in the boundary layer. The constant amount of gas thus appears as a constant pressure intercept, independent of the specific activity in the chamber.

Let us now establish the connection between the measured slope of the Overhoff signal and the specific activity of a gas. Consider the following analysis for two pressures, p_1 and p_2, within the linear response regime for a gas sample of known activity. The measured pressure intercept is p_0, and R is the gas constant in appropriate units.

Chamber volume (m^3):	V	
Chamber temperature (K):	T	
Specific activity (Ci/mol):	A	
Pressure (torr):	p_1	p_2
Moles of gas (mol):	$n_1 = p_1 \cdot V/(R \cdot T)$	$n_2 = p_2 \cdot V/(R \cdot T)$
Activity in cell (Ci):	$A \cdot n_1$	$A \cdot n_2$
Activity density (Ci/m^3):	$a_1 = A \cdot n_1/V$	$a_2 = A \cdot n_2/V$
Signal observed (Ci/m^3):	S_1	S_2

Slope (Ci/m^3/torr)

from Activity:

$$m_A = (a_2-a_1)/(p_2-p_1)$$
$$m_A = A/(R \cdot T)$$

from Signal:

$$m_S = (S_2-S_1)/(p_2-p_1)$$
$$m_S = S_1/(p_1-p_0)$$
$$m_S = S_2/(p_2-p_0)$$

In the linear regime the two slopes, m_A and m_S, must be identical within a calibration factor, F.

$$m_A = F \cdot m_S$$

Thus, the specific activity is given by

$$A = F \cdot m_S \cdot R \cdot T$$

While A here is in units of curies per mole (of all hydrogen isotopes), another useful unit for specific activity is parts per million of moles of tritium (as atoms) in moles of hydrogen (as atoms, all isotopes). The conversion factor is given by the activity of one mole of tritium atoms,

$$1 \text{ mol(T)} = \lambda \cdot N_A/(3.7 \times 10^{10}) \text{ Ci}$$

where $\lambda = \log_e 2/t_{\frac{1}{2}}$ is the decay constant of tritium and $t_{\frac{1}{2}}$=3.891 $\times 10^8$ s is its half-life [4], and N_A=6.022045 $\times 10^{23}$ is Avogadro's number. Thus, the decay constant, λ, is 1.781 $\times 10^{-9}$ s^{-1} so that

$$1 \text{ mol(T)} = 2.899 \times 10^4 \text{ Ci}$$

or

$$1 \text{ Ci} = 3.449 \times 10^{-5} \text{ mol(T)}.$$

The activity in parts per million is

$$A \text{ (ppm)} = A \text{ (Ci/mol)} \times 3.449 \times 10^{-5} \text{ (mol/Ci)} \times 10^6$$

$$= F \cdot m_S \text{ (Ci/m}^3\text{/torr)} \cdot (760/101325) \text{ (torr/Pa)} \cdot 8.31451 \text{ (J/mol/K)} \cdot T \text{ (K)} \cdot 34.49$$

$$A \text{ (ppm)} = F \cdot m_S \cdot T \cdot 2.151$$

In summary then, the Overhoff signal S is a linear function of pressure p given by

$$S = m_s \cdot (p - p_0)$$

where m_s is the slope and p_0 is the pressure intercept. A weighted least-squares linear fit to the signal as a function of pressure, between 30 and 400 torr, yields the slope. The specific activity is proportional to the slope. Thus, for relative measurements only the slope is needed, and units of V/torr are convenient. The slope can be determined without setting the zero level precisely on the Overhoff and the pressure gauge. Provided the span of these two instruments reads correctly, the zero offsets do not influence the determination of the slope. Furthermore, relative activity determinations do not require the conversion to units of specific activity, provided all measurements are taken at the same temperature.

5. LIMITS OF ACTIVITY MEASUREMENT

Based on the pressure limits of the linear response regime and on the limits of the signal reading on the front panel, we can estimate the limits of activity that the Overhoff can measure. For the minimum activity, assume a maximum reading of 0.2 on the lowest scale, or 0.002 Ci/m^3, at the maximum pressure of 400 torr. This corresponds to about 0.003 ppm, taking F as 1.0 and the temperature as 295 K. For the maximum possible activity, assume a maximum reading of 1.0 on the highest scale, or 1.0 Ci/m^3, at a minimum pressure of 60 torr for reasonable accuracy. Under the further assumption that the pressure intercept is 10 torr, the maximum possible activity is just under 13 ppm. Thus, the dynamic range of the Overhoff is over 4000, providing measurements of activity between 0.003 to 13 ppm, which covers the range of interest for our research on laser-based tritium separation.

6. LEAST SQUARES FITTING

A worksheet in Symphony, OVERHOFF.WR1 (available from the author), has been set up to use the method of Lybanon [5] for fitting the Overhoff signal as a function of pressure. There are five windows in this worksheet: MAIN, RESIDUAL, SIGNAL, SMALL, and DATAIN. Before proceeding, it is important to verify that repeated use of the **F6** key cycles through the first four windows listed above and in that order. While sitting in the MAIN window, a data set is entered into the spreadsheet in a blank area below row 40 in three adjacent columns. For example, the data set for the signal plots of Fig. 1 is listed in Table I. In the first two cells of the first column put labels to identify the data set. The first label will appear in the graphs created later. Beginning in the third row of the data set, put the pressure, the Overhoff signal either in Volts or Ci/m^3, and the estimated absolute error in the Overhoff signal. Error estimates for the pressure readings are already incorporated in the spreadsheet.

After the data set has been entered into the spread sheet place the pointer on the top label of the data set (top cell of the first column). Calculation proceeds through the use of macro commands stored in the spreadsheet. A summary of the macro commands appears in Appendix A. Note that the worksheet environment must include the STAT.APP application before proceeding. This is usually done automatically in the configuration when Symphony is invoked. The first macro, labeled "**a**", is called by using the **F7** key, i.e. **F7**, **a**, **Enter**. The "**a**" macro copies the new data set into the working space at the top of the worksheet, initializes the additional columns used in the calculation, and finds an initial solution to the linear fit with the linear regression function of Symphony. When these manipulations are finished the pointer is left in cell **L1** at the top left of the screen in the MAIN window. The data set appears in the three rightmost columns, **Q**, **R**, and **S**, as shown in Fig. 2.

The initial solution must be iterated until cell **N10** is equal to cell **O10**. These two cells calculate the reduced χ^2 in different ways. When they converge the solution has converged. To iterate the solution press **Alt-s**. After convergence, graphs of the residuals and the fit to the signals will be

Table I

A typical set of Overhoff data displayed in the proper format for analysis in the Symphony spreadsheet, OVERHOFF.WR1.

aug 23/83			⇐ top label
very first			⇐ second label
793	0.3	0.005	⇐ pressure, signal, error in signal
625	0.25	0.005	(torr), (volts), (volts)
491	0.2	0.005	
385	0.16	0.005	
302	0.125	0.005	
237	0.1	0.005	
186	0.077	0.0005	
146	0.059	0.0005	
114	0.045	0.0005	
90	0.034	0.0005	
70	0.026	0.0005	
55	0.0195	0.0005	
43	0.014	0.0005	
33	0.0105	0.0005	
27	0.0076	0.0001	
21	0.0054	0.0001	
16.4	0.0038	0.0001	
12.8	0.0026	0.0001	
9.9	0.0018	0.0001	
7.8	0.0013	0.0001	
6.0	0.0009	0.0001	
3.6	0.0004	0.0001	

created by pressing **Alt-g**. The residual plot is automatically displayed in the RESIDUAL window, *e.g.* as in Fig. 3. Four lines of information are superimposed on the plot. The first line is the first label of the data set as it appears in the worksheet. The second line gives the number of points used in the fit, and the reduced χ^2 of the fit. The third line lists the axis intercepts, first the Overhoff signal intercept with the power of 10 in parentheses, and then the pressure intercept. The last line gives the slope of the linear fit followed by the estimated error in the slope calculated from the fit. The power of 10 in parentheses after the slope applies to the error too. The slope error is not a reliable estimate of the error. Instead the error must be estimated from repeated measurements (see below). By pressing **F6** the display will change to the SIGNAL window showing the best-fit straight line and the data points again with the four lines of information, as shown in Fig. 1(a). Pressing **F6** twice more returns the display to the MAIN window.

The position of the information lines in the residual and signal plots is computed automatically, but it may not always be in a clear area. The last four rows in columns **A** to **G** correspond to the information lines in the plots. Column **A** holds the x-axis coordinates, columns **E** and **F** hold the y-axis coordinates for the signal and residual plots, respectively. The values in column **A** and **E** are computed on the assumption that the minimum values of the pressure and signal are zero. The values in column **F** are spaced evenly above a minimum value, controlled by the entry in cell **I9**. If **I9** is zero then the most negative residual is the minimum value. If **I9** is non-zero then **I9** is the minimum value.

At this point, it may be desirable to eliminate one or more points from the fit and see what affect that has on the fit. This procedure is simplified by the use of another window, DATAIN. While sitting in MAIN with **L1** as the top left cell, press **Alt-d** to change the display to the DATAIN window.

The DATAIN window is exactly the same as MAIN as you left it except that the far right column is now column AL, as shown in Fig. 4. Furthermore, pointer movement is restricted to the cells in AL below the title. The entries in this column should all be 1. By changing any of these entries to 0, the corresponding data points will be eliminated from the fit. Take care that at least two points are left in the fit. To prepare for the new linear fit, first return to MAIN by hiding DATAIN and cycling through the other windows: press **Alt-h**. Now press **Alt-i** to initialize the data columns and calculate the new initial solution with the built-in regression function. From here on the calculation proceeds as before by pressing **Alt-s** to iterate the solution. For example, Fig. 5 shows the MAIN window for the data set of Table I after the solution converged for a subset of the data as given in Fig. 4. This time the plot of residuals will display two sets of symbols: an open square as before for the points included in the fit, and a cross for points excluded from the fit, as shown in Fig. 3. In the SIGNAL window, however, the points are still all plotted with one symbol as in Fig. 1. After you have finished all manipulations with the data set, check that at least the top two entries below the title in the AL column in the DATAIN window are set to 1. If this is not done then calculations on the next data set will not work because all data points will be excluded. The current limit on the number of data points is 38, but usually 6 to 10 is sufficient.

7. CALIBRATION OF BACK-PANEL OUTPUT

While the units of V/torr are practical and convenient, the conversion from V/torr to Ci/m^3 is sometimes required. Analysis of the DVM measurements as a function of the front panel signal provides a conversion factor of 0.14963±0.00014 (standard error of the mean, 1 standard deviation is 0.00205) $V/(Ci/m^3)$ for the 1 Ci/m^3 scale. This is the average of 215 data pairs from the sets DS#8 to DS#28, excluding two extreme points and all signals less than 0.1 on the 0.01 Ci/m^3 scale of the Overhoff. Note that full scale at the back panel for any of the three front panel scale settings corresponds to about 6.7 V, thus the conversion factor for the 0.1 Ci/m^3 scale is 0.014963 $V/(Ci/m^3)$ and for the 0.01 Ci/m^3 scale is 0.0014963 $V/(Ci/m^3)$. The 215 data pairs are distributed between 25 and 500 torr with most pairs falling below 200 torr. The data sets consist of low activity samples uniformly distributed between 0.001 and 0.025 Ci/m^3. As the data pairs of DS#2 consisted of much higher activity, ranging from 0.008 to 0.9 Ci/m^3, they were not included in the calculation of the conversion factor. An estimate of the conversion factor from DS#2 alone is 0.150±0.002 (1 standard deviation) $V/(Ci/m^3)$ from 9 data pairs. This conversion factor is consistent with the first one, but there is no need to combine the two at the moment. Indeed, as most of the work with the Overhoff involves measuring a relative change in activity, there is no need to convert the voltage levels to activity. Until a good absolute calibration can be performed, the activity scale itself is only approximate.

8. ABSOLUTE CALIBRATION

The Overhoff is calibrated for tritium in air but its response to CF_3T in CF_3H is similar. There have been two indirect calibrations of the absolute scale of the Overhoff. The first was based on a sample of CF_3T made here at Research Division in July 1983 and then measured 23 August 1983. The second calibration results from a sample of CF_3T manufactured by Amersham in February 1987 and then measured 16 February 1988 as DS#2. For both samples, the synthesis of CF_3T involved equilibrating the hydrogen exchange of gaseous CF_3H with a liquid mixture of tritiated water, sodium hydroxide, and dimethyl sulfoxide. The difference in the two samples lies in their activity and perhaps their chemical purity. For the first sample, we estimated the CF_3T concentration at 0.33 ppm from knowing the initial activity in the liquid solution and from estimating the exchange constant. The measurement on the Overhoff and subsequent analysis yielded 0.28±0.01 ppm.

The sample from Amersham was provided in a break-seal glass vial containing nominally 8 mCi of CF_3T. We diluted the contents of the vial into 5 ℓ-atm of CF_3H stored in a 500 ml steel cylinder in the Radiation Materials Laboratory. (Two other identical cylinders are also stored in the RML. One contains nominally 8 mCi of CF_3T, and the other contains nominally 25 mCi, each diluted in 5 ℓ-

atm of CF_3H. The radioactivity was determined by Amersham at the time of manufacture, mid-February 1987, and not checked independently. (See the report by Dr. J.R. Robins [2] for a comparison of our analysis of this gas on a radiographic gas chromatograph with that of Amersham.) The concentration calculated from 8 mCi in 5 ℓ-atm is 1.34 ppm, which decays to 1.27 ppm after one year. On the Overhoff we measured the concentration of this mixture at 1.39±0.01 ppm.

Although neither of these comparisons provides a proper calibration, they clearly show that the Overhoff measurement gives the correct order of magnitude and probably lies within 20%. An independent calibration would require measuring a sample of CF_3T by a different technique, such as radiographic gas chromatography or liquid scintillation counting. We have tried the former [2] and are not satisifed with the accuracy provided by the flow proportional counters currently available for the activity measurements. The difficulty with liquid scintillation counting is that CF_3H is relatively insoluble in most of the counting liquids. This type of calibration has not yet been attempted.

9. ERROR ESTIMATE

The worksheet, OVERHOFF.WR1, provides an internal estimate of the error in the calculated slope. A better estimate of error in the slope measurements is found by repeated measurements on the same sample. On 10 November 1988 the stock CF_3T was sampled three times. The measured slopes, neglecting factors of 10, were 3.544, 3.558 and 3.546. The average value is 3.549 with a maximum deviation of 0.009 or 0.25%.

10. LINEARITY TEST

The theory of the Overhoff implies that the response is linear with the activity of the gas sample. To test the linearity we measured the activity of a stock sample of CF_3T, then diluted the sample with pure CF_3H by a factor of 3 in concentration and measured the activity again. The activity of the diluted sample corrected for the dilution factor was 1.7% lower than the activity of the initial sample. The dilution factor was obtained from a ratio of pressures and the errors in the pressure measurements were about 0.5%. This test, however, was performed during the time that the Overhoff had a significant baseline from a residual signal (see below), thus the measured signals were corrected for the pressure dependent baseline. Immediately after this the Overhoff was disassembled and cleaned. Allowing for additional errors arising from the baseline, the Overhoff response is linear with activity. It may be of interest to conduct further tests of the linearity at a later date.

11. PRESSURE INTERCEPT

The utility of the slope method for evaluating the activity of a gas sample does not rely on the pressure intercept being a constant. It is, however, interesting to examine how the intercept has varied. For the 20 data sets, DS#8 through DS#28 excluding DS#21, the average pressure intercept was computed. The result is 10.94±0.96 torr (1 standard deviation), with a slight trend to increasing intercept from DS#8 to DS#28. The activities for those 20 runs were in the range of 0.032 to 0.039 ppm. In DS#2 the Amersham sample at 1.39 ppm had a pressure intercept of 7.9 torr. In the dilution test of linearity the pressure intercepts were 12.3 and 12.4 torr, while the activity changed by a factor of 3. Although the spread is fairly large, all the intercept values lie in the vicinity of 10 torr, independent of the activity of the gas sample. In several later dissociation runs, however, the activity measured before dissociation generally had a slightly higher intercept than the activity measured after dissociation. There may be some bias in these measurements as a result of changes in the gas composition with dissociation, e.g. with the production of C_2F_4. This has not been tested but may be another aspect of the interesting problem of the source of the pressure intercept. A complete theory of the proportional counter would solve this problem.

12. RESIDUAL ACTIVITY ON NEW GAS RACK

In June 1988, most of the gas rack was replaced to remove a problem of oil contamination and to simplify the connections between the gas supply bottles, the dissociation cell and the Overhoff. The valve and tube to the Overhoff was not replaced, but only re-attached to the new rack section. Testing the Overhoff on the new gas rack revealed a problem of residual activity, i.e. a signal was obtained by filling the Overhoff with pure nitrogen or CF_3H. While rebuilding the gas rack some surface oil in the tube to the Overhoff must have evaporated from the heat of glassblowing and deposited in the Overhoff chamber. As the bulk of the oil removed from the gas rack had contained tritium, this surface oil must also have been radioactive. The residual signal was reduced by disassembling the cell, cleaning it thoroughly with a degreasing solvent (trichloroethylene), and replacing the connecting tube. Some residual signal remains but it is small and relatively constant with CF_3H pressure: using the 0.01 Ci/m^3 scale the back panel signal is 0.079±0.011 V (3 standard deviations for 12 points) between 30 and 600 torr. With time this residual signal will diminish further. Note that as the baseline is essentially independent of pressure now, it can be neglected in evaluating the slope of the signal response as a function of pressure.

13. CHECK OF CF_3T STOCK

Almost all the work with CF_3T since 1984 has been conducted with a stock supply maintained in a 500-ml steel cylinder. We have measurements of the CF_3T activity in the stock cylinder over a period of five years as listed in Table II. A least squares fit to the natural logarithm of 13 of these measurements as a function of time yields a decay constant of $1.797 \pm 0.106 \times 10^{-9}\ s^{-1}$, shown in Fig. 6 as the dashed line. This value lies within 0.84% of the tritium decay constant of $1.781 \times 10^{-9}\ s^{-1}$, shown as the solid line in Fig. 6. As the decay constant of tritium is independent of chemical bonding, we conclude that the Overhoff has been working correctly and consistently to better than 1% over this period. Routine maintenance during this time, including replacement of the dessicator tube and complete disassembly to clean the chamber, has preserved its response characteristics. The 6% random error in the measured decay constant probably arises from variations in gas transfer between the stock supply and the gas rack. Obviously, the technique developed for measuring activity is proven correct by this measurement of the decay constant of tritium.

Table II

Activity measurements of stock supply of CF_3T.

Date	Activity (ppm)
09-Apr-84	0.0446
15-Aug-86	0.0389
22-Aug-86	0.0378
22-Oct-86	0.0381
24-Mar-87	0.0388
16-Feb-88	0.0352
12-Jul-88	0.0348
21-Oct-88	0.0339
04-Nov-88	0.0338
10-Nov-88	0.0337
17-Nov-88	0.0340
17-Apr-89	0.0340
18-Apr-89	0.0339

14. CONCLUSIONS

The Overhoff is a reliable and reproducible instrument for measuring the activity of CF_3T in CF_3H. The signal response is a linear function of pressure in the range of 30 to 400 torr. Thus, the most effective method of measuring the activity of a gas sample requires a record of the Overhoff signal as a function of the pressure in this range. A weighted least-squares linear fit to the data in the Symphony spreadsheet OVERHOFF.WR1 yields the slope of the function. The specific activity, A, is proportional to the slope and is obtained in units of parts per million by the formula

$$A = F \cdot m_s \cdot T \cdot 2.151$$

where m_s is the measured slope of the signal in Ci/m^3/torr, T is the absolute temperature of the chamber in K_s and F is the as yet unknown absolute calibration factor to relate the Overhoff signal units of Ci/m^3 to real units of Ci/m^3. For now we take F as 1.0 with an error of ±20%. Most of the work with the Overhoff involves measuring changes in activity. These relative measurements do not require conversion to absolute units of specific activity, either ppm or Ci/mol. The only current need for a better absolute calibration of the Overhoff is for more accurate monitoring of the total radioactivity of CF_3T in the laboratory.

Usually the slope is measured in units of V/torr based on reading the voltage signal from the back panel with a DVM. The conversion factor is 0.14963 V/(Ci/m^3) multiplied by the front panel scale setting, i.e. 1 or 0.1 or 0.01. For example, if the front panel is set to 0.1 Ci/m^3 then the conversion factor for the back panel voltage is 0.014963 V/(Ci/m^3).

Measuring the slope of the linear response provides an important operational advantage: precise setting of the zero of the Overhoff and the zero of the pressure gauge is not required. As long as the span of response of these two instruments is unchanged by the zero setting, the slope measurement cancels any zero offsets.

Gas samples of CF_3T in CF_3H with activity in the range of 0.003 to 13 ppm can be measured with a precision of less than 0.5% on a minimum sample size of 5000 torr-ml. This range completely overlaps the activity range of interest in our research on laser-based tritium separation.

Approved:

GL. Fn
for
A.F. Baljet
Manager
Electrical Research Department

Submitted:

Hugh Morrison

H.D. Morrison
Physicist
Science Section
Electrical Research Department

HDM/HDM/CB

REFERENCES

1. F.E. Bartoszek, K.E. Donnelly, K.M. Kalyanam, H.D. Morrison, J.A. O'Neill, J.R. Robins, S.K. Sood, K.B. Woodall, and O.K. Kveton, "Laser-Based Hydrogen Isotope Separation System for Large-Scale Applications" in *Fusion Technology 1988*, A.M. Van Ingen, A.Nijsen-Vis, H.T. Klippel (editors), (Elsevier Science Publishers B.V., 1989), pp. 1317-1321.

2. J.R. Robins, "Analysis of CF_3T Radiochemical Purity", Research Report E89-15-K.

3. W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, *Numerical Recipes: The Art of Scientific Computing*, (Cambridge University Press, 1986) pp. 502-503.

4. M. Lybanon, "A better least-squares method when both variables have uncertainties", Am. J. Phys. *52*, 22-27 (1984).

5. C.M. Lederer and V.S. Shirley (Eds), *Table of Isotopes, 7th ed.*,(John Wiley, New York, 1978).

APPENDIX A

Summary of SYMPHONY macro commands in OVERHOFF.WR1

Key Sequence	Description
F7,a,Enter	Function: Copies a data set into the working area, initializes the other columns, finds an initial solution. To use: Sit in MAIN with pointer on the top label of the data set.
Alt-d	Function: Change display from MAIN to DATAIN, to enable changes in column AL. To use: Sit in MAIN with L1 as the top left cell.
Alt-g	Function: Create graph of residuals and graph of fit. To use: Sit anywhere in MAIN.
Alt-h	Function: Hide DATAIN and return to MAIN. To use: Sit anywhere in DATAIN.
Alt-i	Function: Initialize the data columns and find a new initial solution. To use: Sit anywhere in MAIN.
Alt-s	Function: Solve the next iteration of the least-squares fit. To use: Sit anywhere in MAIN. Usually the pointer will be in the top left corner in L1.

FIGURE CAPTIONS

1. Overhoff signal as a function of pressure from the data set listed in Table. I. The line is the weighted least-squares best fit calculated in the Symphony spreadsheet OVERHOFF.WR1, based on the 11 data points that lie between 30 and 400 torr. Note the saturation of the signal at high pressure. The inset reveals the positive pressure intercept of the line near 10 torr. The legend in the lower right is explained in Section 6. This graph, without the inset, appears in the SIGNAL window of the spreadsheet.

2. Appearance of the MAIN window in OVERHOFF.WR1 after using the "a" macro on the data set of Table I. The two labels of the data set appear in cells **N6** and **N7**. All 22 data points are included in this initial solution. Cells **N10** and **O10** calculate the reduced χ^2 of the linear fit by different formulas.

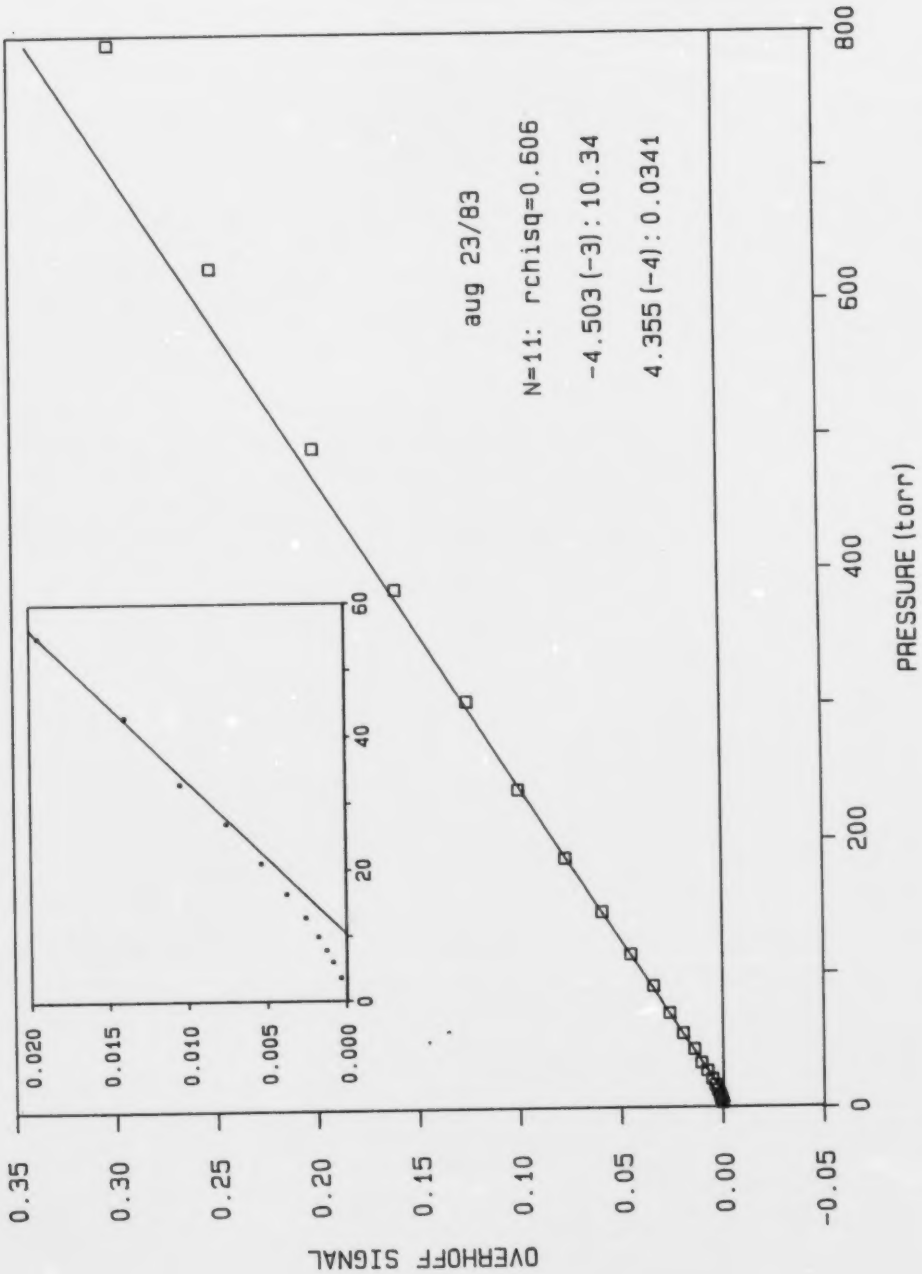
3. The residuals as a function of pressure for the linear fit to the Overhoff signal shown in Fig. 1. The squares indicate points used in the fit (N=11) and the crosses indicate points excluded from the fit. The legend in the lower right is the same as in Fig. 1 and explained in Section 6. The sideways S-shape of the residuals is typical, indicating a cubic dependence of the signal as a function of pressure. A cubic fit, however, does not have a simple interpretation like the linear fit.

4. Appearance of the DATAIN window in OVERHOFF.WR1 after removing the high and low pressure points from the fit as indicated in column **AL**. Note the reduced number of observations and degrees of freedom in cells **P15** and **P16**.

5. Appearance of the MAIN window in OVERHOFF.WR1 after iterating the solution 4 times. The reduced χ^2 values calculated in cells **N10** and **O10** have converged. Cell **N3** contains the slope (a2) and cell **N5** contains the pressure intercept (-a1/a2). The estimate of the standard error in the slope calculated from the residuals appears in cell **N9**.

6. A least-squares fit to the natural logarithm of the activity of the CF_3T stock supply (see Table II) as a linear function of time reveals a decay constant of $1.797 \pm 0.106 \times 10^{-9}\ s^{-1}$, shown as the dashed line. This overlaps the known value of the tritium decay constant (see text and Ref. 5), $1.781 \times 10^{-9}\ s^{-1}$, shown as the solid line passing through the first point.

FIGURE 1


aug 23/83
N=11: rchisq=0.606
-4.503 (-3) : 10.34
4.355 (-4) : 0.0341
OVERHOFF SIGNAL
PRESSURE (torr)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
0
200
400
600
800
0.020
0.015
0.010
0.005
0.000
0
20
40
60

L1:

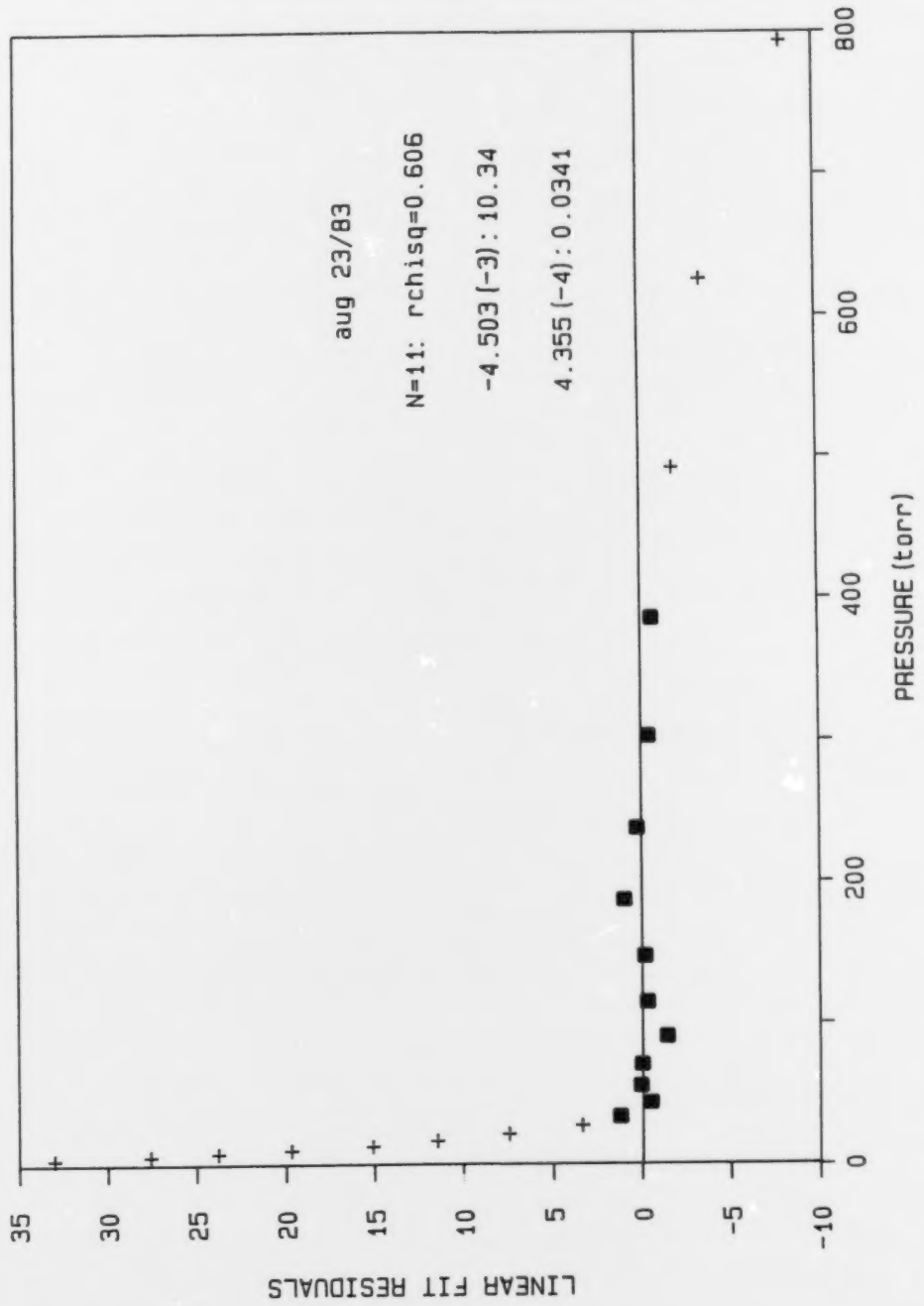
SHEET

	L	M	N	O	P	Q	R	S
1		initial	est	da	new x.ini		y.ini	sigma.y
2	a1	-0.00066	-0.000667	-1.6E-03	-0.002269	793	0.3	0.005
3	a2	0.000396	0.0003969	6.8E-06	4.04E-04	625	0.25	0.005
4			p.int			491	0.2	0.005
5	A11	8.2E+08	1.68		iteration	385	0.16	0.005
6	A12	1.3E+10	aug 23/83	0	1	302	0.125	0.005
7	A22	5.9E+11	very first		S	237	0.1	0.005
8	B1	-1222505	std.err.a2		2.46E+03	186	0.077	0.0005
9	B2	-1.7E+07	1.63E-06		2.46E+03	146	0.059	0.0005
10	Reduced.chisq		119.44471	122.96079	0.00E+00	114	0.045	0.0005
11		Regression Output:				90	0.034	0.0005
12	Constant			-0.000667	3.6	70	0.026	0.0005
13	Std Err of Y Est			0.0046516	793	55	0.0195	0.0005
14	R Squared			0.9973456		43	0.014	0.0005
15	No. of Observations			22	22	33	0.0105	0.0005
16	Degrees of Freedom			20	20	27	0.0076	0.0001
17						21	0.0054	0.0001
18	X Coefficient(s)	0.0003969				16.4	0.0038	0.0001
19	Std Err of Coef.	0.0000045				12.8	0.0026	0.0001
20						9.9	0.0018	0.0001

MAIN

FIGURE 2

FIGURE 3


aug 23/83
N=11: rchisq=0.606
-4.503(-3): 10.34
4.355(-4): 0.0341
LINEAR FIT RESIDUALS
PRESSURE (torr)
35
30
25
20
15
10
5
0
-5
-10
0
200
400
600
800

AL2: 0 SHEET

	L	M	N	O	P	Q	R	AL
1		initial	est	da	new	x.ini	y.ini	data.in
2	a1	-0.00066	-0.000667	-3.8E-03	-0.004503	793	0.3	0
3	a2	0.000396	0.0003969	3.9E-05	4.36E-04	625	0.25	0
4			p.int			491	0.2	0
5	A11	32099845	1.68		iteration	385	0.16	1
6	A12	3.0E+09	aug 23/83	0	1	302	0.125	1
7	A22	3.6E+11	very first		S	237	0.1	1
8	B1	-7939.90	std.err.a2		1.36E+02	186	0.077	1
9	B2	2576959.	3.41E-06		2.46E+03	146	0.059	1
10	Reduced.chisq		15.04410	15.06228	2.32E+03	114	0.045	1
11		Regression Output:				90	0.034	1
12	Constant			-0.000667	3.6	70	0.026	1
13	Std Err of Y Est			0.0046516	793	55	0.0195	1
14	R Squared			0.9973456		43	0.014	1
15	No. of Observations			22	11	33	0.0105	1
16	Degrees of Freedom			20	9	27	0.0076	0
17						21	0.0054	0
18	X Coefficient(s)	0.0003969				16.4	0.0038	0
19	Std Err of Coef.	0.0000045				12.8	0.0026	0
20						9.9	0.0018	0
								DATAIN

FIGURE 4

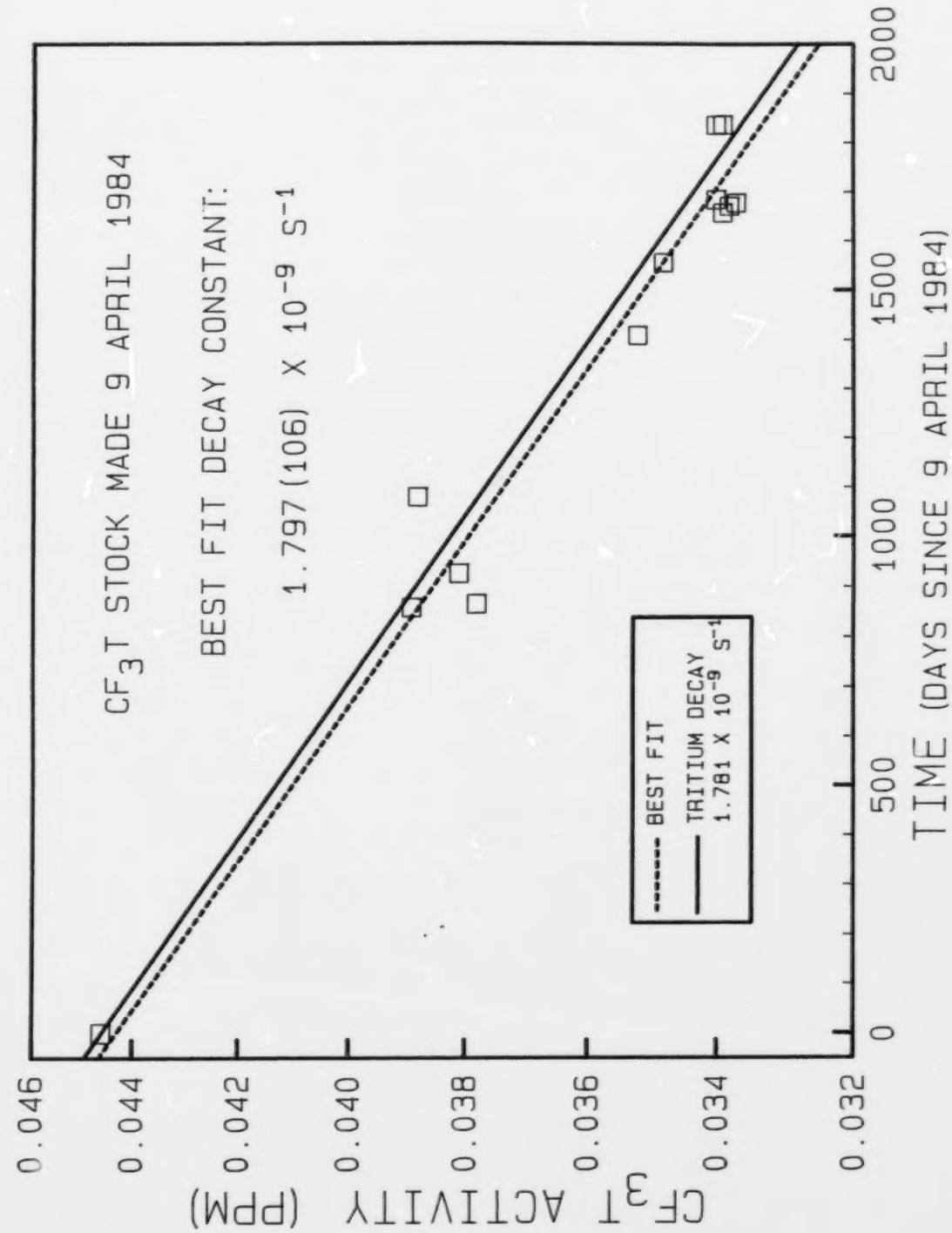
L1: SHEET

	L	M	N	O	P	Q	R	S
1		initial	est	da	new	x.ini	y.ini	sigma.y
2	a1	-0.00066	-0.004503	1.1E-13	-0.004503	793	0.3	0.005
3	a2	0.000396	4.36E-04	-1.2E-15	4.36E-04	625	0.25	0.005
4			p.int			491	0.2	0.005
5	A11	32095737	10.34		iteration	385	0.16	0.005
6	A12	3.0E+09	aug 23/83	4	5	302	0.125	0.005
7	A22	3.6E+11	very first		S	237	0.1	0.005
8	B1	0.000000	std.err.a2		5.46E+00	186	0.077	0.0005
9	B2	-0.00010	3.41E-06		2.46E+03	146	0.059	0.0005
10	Reduced.chisq		0.60627	0.60627	2.45E+03	114	0.045	0.0005
11		Regression Output:				90	0.034	0.0005
12	Constant			-0.000667	3.6	70	0.026	0.0005
13	Std Err of Y Est			0.0046516	793	55	0.0195	0.0005
14	R Squared			0.9973456		43	0.014	0.0005
15	No. of Observations			22	11	33	0.0105	0.0005
16	Degrees of Freedom			20	9	27	0.0076	0.0001
17						21	0.0054	0.0001
18	X Coefficient(s)	0.0003969				16.4	0.0038	0.0001
19	Std Err of Coef.	0.0000045				12.8	0.0026	0.0001
20						9.9	0.0018	0.0001

MAIN

FIGURE 5

FIGURE 6



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